Naval Surface Warfare Center
Carderock Division
West Bethesda, MD 20817-5700

NSWCCD-65-TR–2004/10 April 2004

Survivability, Structures, and Materials Department

Technical Report

Effects of Single Wall Carbon Nanotubes on Interlaminar Shear in GRP Panels

by

Robert C. Matteson and Roger M. Crane

NSWCCD-65-TR–2004/10 Effects of Single Wall Carbon Nanotubes on Interlaminar Shear in GRP Panels

DEPARTMENT OF THE NAVY
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From: Commander, Naval Surface Warfare Center, Carderock Division
To: Chief of Naval Research (ONR 332)

Subj: CARBON SINGLE WALLED NANOTUBE (SWNT) PROGRAM

Ref: (a) Seaborne Structures Materials Program (PE 0602236N)

Encl: (1) NSWCCD-65-TR–2004/10, *Effects of Single Wall Carbon Nanotubes on Interlaminar Shear in GRP Panels*

1. Reference (a) requested the Naval Surface Warfare Center, Carderock Division (NSWCCD) to participate with Rice University to investigate the use of carbon SWNT as a means to provide enhanced interlaminar shear strength in 24-oz, E-glass woven roving /vinyl ester composites. Enclosure (1) summarizes the short beam shear testing of glass reinforced plastic (GRP) specimens consisting of 24-ounce woven roving e-glass and vinylester. The panels consisted of 12 plies of the woven roving where only the center two plies had various surface modified carbon SWNT applied to them. This was done due to the cost and limited supply of the carbon SWNTs.

2. Comments or questions may be referred to Dr. Roger M. Crane, Code 655; telephone (301) 227-5126; e-mail, Roger.Crane@navy.mil.

E.A. RASMUSSEN
By direction

Subj: CARBON SINGLE WALLED NANOTUBE (SWNT) PROGRAM

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Enclosure (1)

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14. ABSTRACT
This report summarizes the testing of glass reinforced plastic (GRP) panels consisting of 24-ounce woven roving e-glass and vinylester. The center two plies of woven roving of each panel have been treated with varying amounts of carbon nanotubes. The purpose of incorporating the carbon nanotubes is to increase the interlaminar shear strength of the composite panel. The Short Beam Shear test was used as a quick screening method to determine the effect of single wall carbon nanotubes (SWNTs) on interlaminar shear strength. It was found that the single walled carbon nanotubes caused a decrease in the interlaminar shear strength for this material system. The decrease in shear strength may be due to a problems with the functionalization of the SWNTs or due to the SWNTs trapping free radicals resulting in incomplete cure.

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ship structures, composite materials

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Administrative Information

The work described in this report was performed by the Structures and Composites Division of the Survivability, Structures, and Materials Department, at the Naval Surface Warfare Center, Carderock Division (NSWCCD). The work was funded by the Office of Naval Research, Code 332, under the Seaborne Structures Materials Program (PE 0602236N) under the guidance of Dr. Ignacio Perez.

Acknowledgements

The authors would like to acknowledge Jiang Zhu from Rice University for his support in the incorporation of the carbon nanotubes onto the E-glass woven roving and in the fabrication and testing of the composite test specimens.

Background

Single-walled carbon nanotubes (SWNTs) have been professed to provide significant mechanical reinforcement for composite materials due to their high strength (50-100 GPa). The strength enhancement potential of using nanotubes in polymer composite to provide reinforcement has not been realized, mainly because of issues such as nonhomogeneous dispersion and poor surface reactivity. [1,2] Chemical functionalization has been successfully used to obtain strong interfacial bonding and homogenous dispersion, so that nanotubes can provide effective load transfer to the matrix. [3]

The purpose of this study was to determine if there is a strengthening effect of SWNTs on the interlaminar shear strength of E-glass woven roving composite specimens. In addition, the effect that functionalization has on enhancing the interlaminar shear strength is investigated. In terms of impact to the Navy, increasing the shear strength of GRP materials may have a significant impact on increasing design allowables for shear and fracture toughness of similar reinforced plastic material systems which are currently under consideration for Navy applications.

Specimen Fabrication

Four composite panels were fabricated using 12 plies of Hexcel 24-ounce woven roving with a warps parallel orientation. Dow Derakane 510A vinylester resin was infused into the glass fabric using the Seemann Composites Resin Infusion Molding Process (SCRIMP) vacuum assisted resin transfer molding method. The fabricated panels were nominally 0.25-inches thick. Each of the panels was treated with varying concentrations of the SWNT. In addition, two of the panels used functionalized SWNT.

Because of the cost and availability of the carbon SWNT, only two plies of each composite panel had carbon SWNT incorporated onto them. The application of the SWNT to the E-glass woven roving was accomplished as follows. First, the SWNT were dispersed in ethanol solution and sonicated for two hours to ensure dispersion. This solution was then sprayed on the surface of E-glass woven roving. After evaporation of the solvents, the remaining nanotubes effectively coated the fabric surface. This overcoat of nanotubes are in intimate contact with the E-glass fibers within the woven roving and should form a thin-film interphase layer between the fiber and matrix. This should provide increased strength through the thickness of the layed composite. The functionalized nanotubes should chemically bond to the fiber while interacting strongly with the matrix. For these plies, the uniform coating of carbon SWNTs was visually observed. The coated plies of fiberglass in this case are gray in appearance instead of the white color of the uncoated E-glass woven roving. The carbon SWNT used in panels 3 and 4 were functionalized using two different methods to try to improve their dispersion within and adhesion to the vinyl ester resin. Panel 3 was functionalized with methacrylate silane (CH2=C(CH3)-COO-CH---) coupling agent. Panel 4 had nanotubes functionalized with allylmagnesiumbromide (CH2=CHCH2MgBr). In both cases the objective is to provide unsaturated carbon double bonds (C=C) which can be polymerized with the vinylester system. This information is summarized in Table 1.

Table 1. Panel Characteristics

Panel #	SWNT Concentration	Functional Agent
1	0%	None
2	0.20%	None
3	0.10%	Silane
4	0.20%	Allyl

To manufacture the composite panels for testing, two plies of the SWNT coated woven roving were placed in the center of 10 plies of uncoated E-glass woven roving. This results in a panel with a midplane that has carbon SWNTs on each surface. The four composite panels were placed on a glass plate arranged in a line. A single vacuum bag was used to process all four panels simultaneously using the same resin batch. A schematic of the panel arrangement and resin flow is shown in Figure 1.

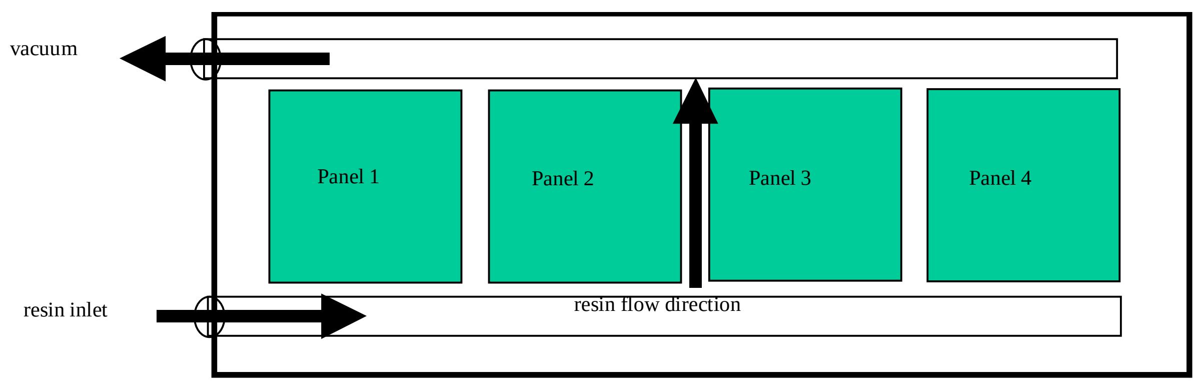

Figure 1. Schematic of SCRIMP Panel Fabrication of Test Panels

Testing

The test panels were manufactured to assess the effect of the SWNT on the interlaminar properties of the E-glass woven roving composites. The interlaminar shear strength was determined using the ASTM D 2344 Short Beam Shear method. The Short Beam Shear method, while not a direct measure of shear properties, is a standard test method used to estimate the shear strength of laminated composite materials.

Ten specimens were machined from each panel to the ASTM D 2344 specifications. All specimens were nominally 0.25-inches wide, 0.25-inches thick, and 1.75-inches long. The support span used in all the tests was 1.25-inches.

Results

Figure 2 summarizes testing results for this study. It shows that, in all cases, the SWNT treatment resulted in a decrease in interlaminar shear strength compared to the untreated panel. The decrease was most significant for the silane-functionalized SWNT, which resulted in a 14% decrease. The non-functionalized SWNT treatment resulted in a 7% decrease in interlaminar shear strength. While the allyl-functionalized SWNT treatment resulted in an apparent decrease in interlaminar shear strength of 3%, this is not significant when compared with the standard deviation for the untreated panels (3.8%).

The effect of functionalization of the SWNT on properties is mixed. It was assumed from the comparison of the nonfunctionalized SWNT to the control, that the addition of a lower weight percent of the SWNT would have resulted in a smaller reduction in interlaminar shear strength. This was not the case. The panel that incorporated a 0.1 weight percent silane modified SWNTs showed a reduction in interlaminar shear strength compared to the panel that had 0.2 weight percent of untreated SWNT. It is not known if these results were caused by poor dispersion or interfacial issues with the SWNT. An investigation of the surface morphology of the failure surface was not carried out.

For the Allyl functionalized SWNT, there was a slight improvement in interlaminar shear strength compared to the nonfunctionalized SWNT.

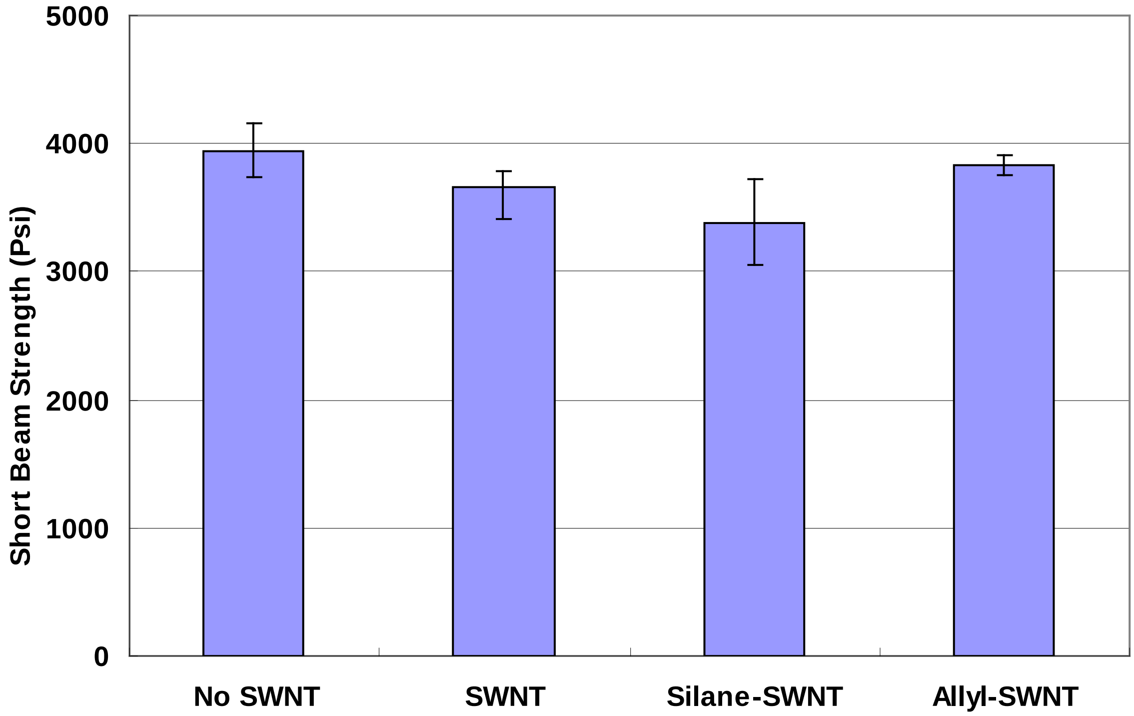

Figure 2. ASTM D2344 - Short Beam Shear Method

Conclusions

The surface treatment of E-glass woven roving with single walled carbon nanotubes did not provide property enhancement but resulted in a decrease in interlaminar shear strength. The silane functionalization used in this study resulted in a decrease in interlaminar shear strength compared to the nonfunctionalized SWNT. The Allyl functionalization resulted in a higher interlaminar shear strength than both the silane functionalized SWNT and the SWNT without functionalization.

It should be noted that none of the panels in this study received post cure treatment. This may be significant, since SWNTs can trap free radicals, which would likely reduce polymerization rate during cure. Subsequent panels, post cured at Rice University and tested at The University of Texas, at Pan America suggest that post curing at 110°C for 8-hours increases the shear strength of the SWNT treated panels by as much as 19%, but still results in no significant increase above untreated panels.

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